

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 342 912  
A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 89304912.2

(22) Date of filing: 16.05.89

(51) Int. Cl.4: C08K 5/00 , C08L 79/08 ,  
/(C08K5/00,5:34),(C08K5/00,  
5:41),(C08K5/00,5:37)

(30) Priority: 17.05.88 JP 118362/88  
18.08.88 JP 203717/88

(43) Date of publication of application:  
23.11.89 Bulletin 89/47

(84) Designated Contracting States:  
CH DE FR GB IT LI NL SE

(71) Applicant: MITSUI TOATSU CHEMICALS INC.  
No. 2-5, Kasumigaseki 3-chome  
Chiyoda-Ku Tokyo 100(JP)

(72) Inventor: Yamaya, Norimasa  
2882, Iijimacho Sakae-ku  
Yokohama-shi Kanagawa-ken(JP)  
Inventor: Ohta, Masahiro  
1541, Yabecho Totsuka-ku  
Yokohama-shi Kanagawa-ken(JP)  
Inventor: Yamaguchi, Akihiro  
1-13-24, Zaimokuza  
Kamakura-shi Kanagawa-ken(JP)

(74) Representative: Stuart, Ian Alexander et al  
MEWBURN ELLIS & CO. 2/3 Cursitor Street  
London EC4A 1BQ(GB)

(54) Thermosetting resin compositions.

(57) The present invention relates to a thermosetting resin composition comprising about 100 parts by weight of a polyimide and from 5 to about 100 parts by weight of a bismaleimide having a similar structure and processes for preparing the same.

EP 0 342 912 A1

## THERMOSETTING RESIN COMPOSITIONS

The invention relates to thermosetting resin compositions and processes for their preparation. Preferred embodiments are thermosetting resin compositions that exhibit excellent heat resistance properties and are useful as adhesive films, laminating materials, and molding materials.

Polyimide resins have conventionally been used widely in the industry due to their excellent heat resistance, electrical insulating properties and chemical resistance properties.

Among polyimide resins, condensation polyimide resins, which are prepared via polyamic acids by reacting a tetracarboxylic dianhydride and a diamine in a polyimide resin, are among the many resins that exhibit excellent properties. They are however accompanied by disadvantages such as high softening points and poor processabilities. Although a thermoplastic polyether imide that has improved processability at the sacrifice of some heat resistance ("Ultem", trade mark; product of General Electric Company) has been known, its heat resistance and chemical resistance are less than satisfactory.

On the other hand, addition-type polyimide resins prepared by polymerizing bismaleimide compounds exhibit excellent thermal properties but are inferior in mechanical strength. It is therefore impossible to form them into films by casting.

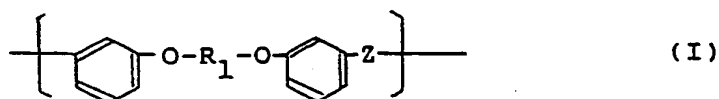
The present invention overcomes the problems and disadvantages of the prior art by providing thermosetting resin compositions that exhibit superior properties.

Preferred embodiments provide thermosetting resin compositions that can be formed into films or the like prior to thermal curing and exhibit excellent toughness, flexibility, adhesion and heat resistance after thermal curing.

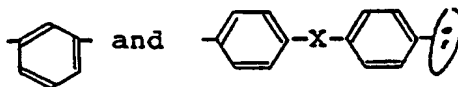
Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention.

The invention provides a thermosetting resin composition comprising:

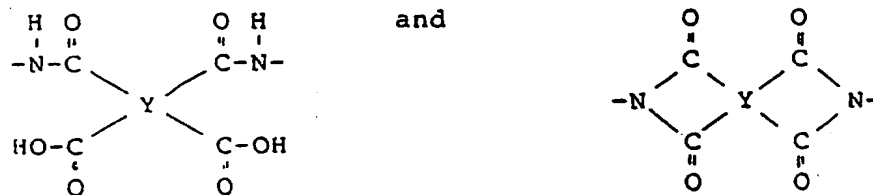
i) about 100 parts by weight of a polymer having recurring units represented by the formula (I):



wherein R<sub>1</sub> represents a divalent group selected from:



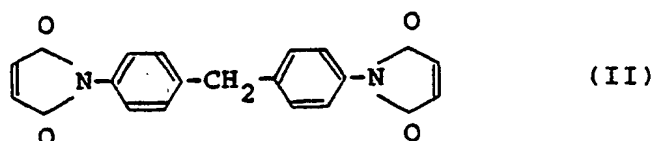
X is selected from a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, a hexafluorinated isopropylidene group, a carbonyl group, a thio group, a sulfinyl group, a sulfonyl group and an oxo group and Z represents at least one of



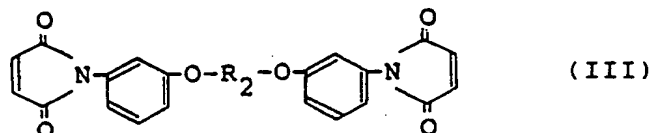
wherein Y represents a tetravalent group selected from:

aliphatic groups having at least two carbon atoms, cycloaliphatic groups, monocyclic aromatic groups, fused polycyclic aromatic groups, and non-fused cyclic aromatic groups composed of aromatic groups bonded together directly or via a crosslink; and

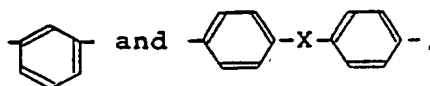
ii) from about 5 to about 100 parts by weight of a bismaleimide compound selected from :  
compounds of the formula (II):



10 and compounds of the formula (III):



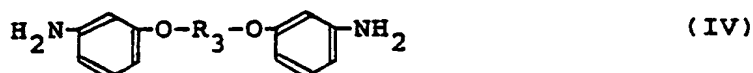
20 wherein R<sub>2</sub> represents a divalent group selected from the group consisting of



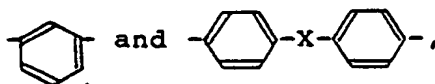
X is selected from: a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, hexafluorinated isopropylidene groups, carbonyl groups, thio groups, sulfinyl groups, sulfonyl groups and oxo groups.

30 Reference will now be made in detail to the present preferred embodiments of the invention.

Preferably, the thermosetting resin composition of the invention contains as a polymer a polyamic acid obtained by reacting (a) a diamine compound represented by the formula (IV):



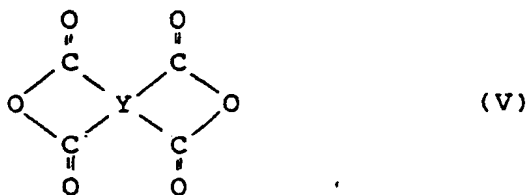
40 wherein R<sub>3</sub> represents a divalent group selected from



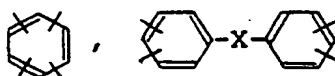
X is selected from a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, a hexafluorinated isopropylidene group, a carbonyl group, a thio group, a sulfinyl group, a sulfonyl group and an oxo group, with (b) at least one tetracarboxylic dianhydride by a method known per se in the art; or (c) a polyimide obtained by dehydrating and cyclizing the polyamic acid.

Exemplary suitable diamine compounds include 1,3-bis(3-aminophenoxy)benzene, bis[4-(3-aminophenoxy)phenyl]methane, 1,1-bis[4-(3-aminophenoxy)phenyl]ethane, 1,2-bis[4-(3-aminophenoxy)phenyl]ethane, 2,2-bis[4-(3-aminophenoxy)phenyl]propane, 2,2-bis[4-(3-aminophenoxy)phenyl]butane, 2,2-bis[4-(3-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 4,4'-bis(3-aminophenoxy)biphenyl, bis[4-(3-aminophenoxy)phenyl] ketone, bis[4-(3-aminophenoxy)phenyl] sulfide, bis[4-(3-aminophenoxy)phenyl] sulfide, bis[4-(3-aminophenoxy)phenyl] sulfone, bis[4-(3-aminophenoxy)phenyl] ether, etc. The diamine compounds may be used either singly or in combination.

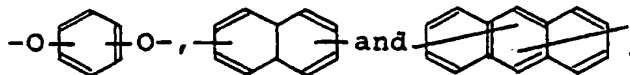
A tetracarboxylic dianhydride is represented by the formula (V):



wherein Y is a tetravalent group selected from aliphatic groups having at least two carbon atoms, cycloaliphatic groups, monocyclic aromatic groups, fused polycyclic aromatic groups, and non-fused cyclic aromatic groups composed of aromatic groups bonded together directly or via a crosslink. Y represents a tetravalent group selected from aliphatic hydrocarbons having from 1 to 4 carbon atoms, cycloaliphatic hydrocarbons having from 4 to 8 carbon atoms,



wherein X is selected from direct bond, aliphatic hydrocarbons having from 1 to 4 carbon atoms, aliphatic hydrocarbons having from 1 to 4 carbon atoms substituted by from 1 to 6 fluorine atoms, -O-, -CO-, -S-, SO<sub>2</sub>-.



Exemplary suitable tetracarboxylic dianhydrides include ethylenetetracarboxylic dianhydride, butanetetracarboxylic dianhydride, cyclopentanetetracarboxylic dianhydride, pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,2',3,3'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, bis(3,4-dicarboxyphenyl) ether dianhydride, bis(3,4-dicarboxyphenyl) sulfone dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, 4,4'-(p-phenylenedioxy)diphthalic dianhydride, 4,4'-(m-phenylenedioxy)diphthalic dianhydride, 2,3,6,7-naphthalenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, 1,2,5,6-naphthalenetetracarboxylic dianhydride, 1,2,3,4-benzenetetracarboxylic dianhydride, 3,4,9,10-perylenetetracarboxylic dianhydride, 2,3,6,7-anthracenetetracarboxylic dianhydride, and 1,2,7,8-phenanthrenetetracarboxylic dianhydride. These tetracarboxylic dianhydrides may be used either singly or in combination.

N,N'-4,4'-Diphenylmethanebismaleimide represented by the formula (II) can be easily prepared by causing 4,4'-diaminodiphenylmethane and maleic anhydride to undergo a condensation and dehydration reaction in a manner known per se in the art.

Other bismaleimide compounds (III) useful in the practice of this invention include 1,3-bis(3-maleimidophenoxy)benzene, bis[4-(3-maleimidophenoxy)phenyl]methane, 1,1-bis[4-(3-maleimidophenoxy)phenyl]ethane, 1,2-bis[4-(3-maleimidophenoxy)phenyl]ethane, 2,2-bis[4-(3-maleimidophenoxy)phenyl]propane, 2,2-bis[4-(3-maleimidophenoxy)phenyl]butane, 2,2-bis[4-(3-maleimidophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 4,4'-bis(3-maleimidophenoxy)biphenyl, bis[4-(3-maleimidophenoxy)phenyl] ketone, bis[4-(3-maleimidophenoxy)phenyl] sulfide, bis[4-(3-maleimidophenoxy)phenyl] sulfoxide, bis[4-(3-maleimidophenoxy)phenyl] sulfone, bis[4-(3-maleimidophenoxy)phenyl] ether, etc. These compounds may be used either singly or in combination.

The bismaleimide compounds can be prepared easily by causing their corresponding diamine compounds and maleic anhydrides to undergo a condensation and dehydration reaction.

With respect to the mixing ratio of the polymer of the formula (I) to the bismaleimide compound, the bismaleimide compound may be used in an amount of from about 5 to about 100 parts by weight, preferably from about 10 to about 80 parts by weight per 100 parts by weight of the polymer of the formula (I). If the proportion of the bismaleimide compound is smaller than about 5 parts by weight, the

bismaleimide compound cannot exhibit the effects of improving processability and mechanical properties, which are intended to be achieved in the present invention. On the other hand, amounts greater than about 100 parts by weight of the bismaleimide compound result in resin compositions which are brittle and have no formability and moldability.

5 Although the mixing of the polymer (I) and bismaleimide compound may be conducted in the form of powders, it is generally conducted by adding and dissolving the bismaleimide compound in a polymer varnish compound, preferably, in a polyamic acid and/or a polyimide varnish or suspension.

Exemplary solvents suitable for use in preparing the polymer varnish or suspension include N,N-dimethylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, N,N-dimethylmethoxyacetamide, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, N-methylcaprolactam, 1,2-dimethoxyethane, bis(2-methoxyethyl) ether, 1,2-bis(2-methoxyethoxy)ethane, bis{2-(2-methoxyethoxy)ethyl}ether, 1,3-dioxane, 1,4-dioxane, pyridine, picoline, dimethyl sulfoxide, dimethyl sulfone, tetramethylurea and hexamethyl phosphoyl amide. These organic solvents may be used either singly or in combination.

The resin composition of the invention can be used as preregs by having base materials such as glass 15 cloths, carbon cloths or the like impregnated therewith, followed by drying. As an alternative, the resin composition can be cast and dried on a glass plate, stainless steel plate or the like so that it can be used as a film-like adhesive free of any base material for various applications. In this case, the drying temperature and time vary depending on the solvent employed and the kind of the bismaleimide used. However, it is necessary to maintain the temperature lower than the temperature at which marked polymerization of the bismaleimide compound begins to take place. The drying time must be long enough to reduce the content 20 of the solvent to at least a level not affecting adversely the objects of this invention.

The resin composition can also be used as is, namely, in the form of powder as a molding material. Although the curing time varies depending on the type of bismaleimide, tough and heat-resistant, molded articles can be obtained by heating and curing molded green products generally under an elevated 25 pressure of from about normal pressure to about 1,000 kg/cm<sup>2</sup> at from about 150 to about 450 °C for from about 0.1 to about 10 hours.

The thermosetting resin composition of this invention may contain a polymerization catalyst if needed. Although no particular limitation is imposed on the amount of the catalyst to be used, preferably the catalyst is employed in an amount of from about 0.001 to about 10 wt.%, more preferably from about 0.1 to about 5 30 wt.% based on the total weight of the materials to be polymerized. Conventional free radical catalysts such as benzoyl peroxide, t-butyl hydroperoxide, dicumyl peroxide, azobisisobutyronitrile and azobiscyclohexane carbonitrile are suitable for use as a polymerization catalyst. Two or more catalysts may be used in combination as needed.

The thermosetting resin compositions of this invention are excellent in adhesion, formability, moldability, 35 flexibility and heat resistance. The thermosetting resin compositions have numerous applications including as adhesives, laminates and molding materials in electrical and electronic equipment and apparatus, and thus have significant industrial utility and advantages.

The invention will be further clarified by the following examples, which are intended to be purely 40 exemplary of the invention.

#### Examples 1-4:

A vessel fitted with a stirrer, a reflux condenser and a nitrogen gas inlet tube was charged with 73.6 g 45 (0.2 mole) of 4,4'-bis(3-aminophenoxy)biphenyl and 467.2 g of N,N-dimethylacetamide. At room temperature, 43.2 g (0.198 mole) of pyromellitic acid dianhydride were added in portions under a nitrogen gas atmosphere while paying attention to any increase of the temperature of the solution. The resultant solution was stirred at room temperature for about 20 hours to obtain a polyamic acid varnish in N,N-dimethylacetamide as a solvent. The varnish had a solution viscosity of 64 poises at 25 °C and a resin 50 content of 20%. The inherent viscosity of the polyamic acid thus obtained was 0.82 dl/g at 35 °C and had a 0.5% resin content.

To 100 g portions of the polyamic acid varnish, N,N'-4,4'-diphenylmethanebismaleimide was added respectively in amounts given in Table 1, followed by the addition of N,N-dimethylacetamide to give a resin content of 20.0%. The components thus added were dissolved at room temperature. Each of the resin 55 compositions thus prepared was cast on a glass plate and then dried at 130 °C for 1 hour and then at 180 °C for 2 hours, both, under a nitrogen gas atmosphere, thereby obtaining an uncured film of 25 μm thick as a soft, brown and transparent film. By heating the uncured film at 250 °C for 30 minutes, a cured tough film was obtained. Table 1 shows the softening points of those uncured films (as measured by the

TMA penetration method) and their tensile shear strengths at 25 °C and a high temperature of 240 °C as measured in accordance with JIS-K-6848 and JIS-K-6850, namely, after separately inserting them between preheated steel sheets (cold rolled steel, JIS-3141, SPEC/SD, 25 x 100 x 1.6 mm) and bonding them to the associated steel sheets at 250 °C under 20 kg/cm<sup>2</sup> for 30 minutes.

Examples 5-8 and Comparative Examples 1-2:

In a similar manner as in Examples 1-4, polyamic acid varnishes were obtained using the diamine compounds and tetracarboxylic dianhydrides Table 1 in their corresponding amounts described in terms of moles in Table 1. In the polyamic varnishes, the bismaleimide compound was then dissolved in the amounts shown in Table 1 to obtain resin composition varnishes. Thereafter, the procedure of Examples 1-4 was followed to obtain the results summarized in Table 1.

Examples 9-12:

A vessel fitted with a stirrer, a reflux condenser and a nitrogen gas inlet tube was charged with 73.6 g (0.2 mole) of 4,4'-bis(3-aminophenoxy)biphenyl and 467.2 g of N,N-dimethylacetamide. At room temperature, 43.2 g (0.198 mole) of pyromellitic acid dianhydride were added in portions under a nitrogen gas atmosphere while paying attention to any increase of the temperature of the solution. The resultant solution was stirred at room temperature for about 20 hours to obtain a polyamic acid varnish in N,N-dimethylacetamide as a solvent. The varnish had a solution viscosity of 64 poises at 25 °C and a resin content of 20.0%. The inherent viscosity of the polyamic acid thus obtained was 0.82 dL/g at 35 °C and had a 0.5% resin content.

To 100 g portions of the polyamic acid varnish, 4,4'-bis(3-maleimidophenoxy)biphenyl was added respectively in amounts given in Table 1, followed by the addition of N,N-dimethylacetamide to give a resin content of 20.0%. The components thus added were dissolved at room temperature. Each of the resin compositions thus prepared was cast on a glass plate and then dried at 150 °C for 1 hour and then at 200 °C for 2 hours, both, under a nitrogen gas atmosphere, thereby obtaining an uncured film of 25 μm thick as a soft, brown and transparent film. By heating the uncured film at 250 °C for 30 minutes, a cured tough film was obtained. Table 1 shows the softening points of those uncured films (as measured by the TMA penetration method) and their tensile shear strengths at 25 °C and a high temperature of 240 °C as measured in accordance with JIS-K-6848 and JIS-K-6850, namely, after separately inserting them between preheated steel sheets (cold rolled steel, JIS-3141, SPEC/SD, 25 x 100 x 1.6 mm) and bonding them to the associated steel sheets at 250 °C under 20 kg/cm<sup>2</sup> for 30 minutes.

Example 13:

Using 41.0 g (0.10 mole) of 2,2-bis[4-(3-aminophenoxy)phenyl]propane as a diamine compound and 30.6 g (0.095 mole) of 3,3',4,4'-benzophenonetetracarboxylic dianhydride as a tetracarboxylic dianhydride, the procedure of Examples 9-12 was repeated in much the same way to obtain a polyamic acid varnish. The varnish was reacted further at 150-160 °C for 16 hours to subject it to dehydration and condensation, thereby obtaining a polyimide varnish having a resin content of 19.2% and a solution viscosity of 74 poises at 25 °C.

To 100 g of the polyimide varnish, 9.6 g of 2,2-bis[4-(3-maleimidophenoxy)phenyl]propane and 20.0 g of N,N-dimethylacetamide were added, followed by dissolution at room temperature. Thereafter, the procedure of Examples 9-12 was repeated in much the same way to obtain the results shown in Table 1.

Examples 13-16:

In a similar manner as in Examples 9-12, polyamic acid varnishes were obtained using the diamine compounds and tetracarboxylic dianhydrides, which are shown in Table 1, in their corresponding amounts described in terms of moles in Table 1. In the polyamic varnishes, the bismaleimide compound was then dissolved in the amounts shown in Table 1 to obtain resin composition varnishes. Thereafter, the procedure of Examples 9-12 was followed to obtain the results summarized in Table 1.

Other embodiments of the invention will be apparent to the skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

5

10

15

20

25

30

35

40

45

50

55

Table 1

	Resin Composition (Parts by weight)				Softening point of uncured film [TMA method] (°C)	Tensile shear strength(kg/cm <sup>2</sup> )	
	Polymer (100 parts)		Bismaleimide compound (parts)	25 °C		240°C	
	Diamine Compound (mole)	Tetracarboxylic dianhydride (mole)					
Ex. 1	4,4'-Bis(3-aminophenoxy)-biphenyl (0.2)	Pyromellitic dianhydride (0.2)	N,N',-4,4'-Diphenylmethane bismaleimide (10)	223	225	145	
Ex. 2	ditto	ditto	ditto (30)	187	252	162	
Ex. 3	ditto	ditto	ditto (50)	169	298	185	
Ex. 4	ditto	ditto	ditto (80)	151	285	180	
Ex. 5	2,2-Bis[4-(3-aminophenoxy)-phenyl]propane (0.1)	3,3',4,4'-Benzophenone-tetracarboxylic dianhydride (0.1)	ditto (50)	176	290	175	



Table I (Cont'd)

	Resin Composition (Parts by weight)				Softening point of uncured film [TMA method] (°C)	Tensile shear strength(kg/cm <sup>2</sup> )	
	Polymer (100 parts)		Bismaleimide compound (parts)	25 °C		240°C	
	Diamine Compound (mole)	Tetracarboxylic dianhydride (mole)					
Ex. 6	Bis[4-(3-aminophenoxy)-phenyl]sulfide (0.1)	Pyromellitic dianhydride (0.1)	N,N'-4,4'-Diphenylmethane bismaleimide (50)	171	285	170	
Ex. 7	ditto (0.1)	3,3',4,4'-Benzophenone-tetracarboxylic dianhydride (0.09)	ditto (50)	169	287	170	
Ex. 8	1,3-Bis(3-aminophenoxy)-benzene (0.1)	ditto (0.098)	ditto (50)	174	290	175	
Comp. Ex. 1	4,4'-Bis(3-aminophenoxy)-biphenyl (0.20)	Pyromellitic dianhydride (0.198)	- (0)	251	250°C	Did not melt so that bonding was not feasible.	
Comp. Ex. 2	ditto	ditto	4,4'-Bis(3-maleimido-phenoxy)biphenyl (120)	No film - forming ability			

Table I (Cont'd)

	Resin Composition (Parts by weight)			Softening point of uncured film [TMA method] (°C)	Tensile shear strength(kg/cm <sup>2</sup> )	
	Polymer (100 parts)		Bismaleimide compound (parts)		25 °C	240°C
	Diamine Compound (mole)	Tetracarboxylic dianhydride (mole)				
Ex. 9	4,4'-Bis(3-aminophenoxy)-biphenyl (0.2)	Pyromellitic dianhydride (0.198)	4,4'-Bis(3-maleimide-phenoxy)biphenyl (10)	213	250	170
Ex. 10	ditto	ditto	ditto (30)	171	275	185
Ex. 11	ditto	ditto	ditto (50)	154	310	210
Ex. 12	ditto	ditto	ditto (80)	144	300	190
Ex. 13	2,2-Bis[4-(3-aminophenoxy)-phenyl]propane (0.1)	3,3',4,4'-Benzophenone-tetracarboxylic dianhydride (0.095)	2,2-Bis[4-(3-maleimido-phenoxy)phenyl]propane (50)	172	305	205

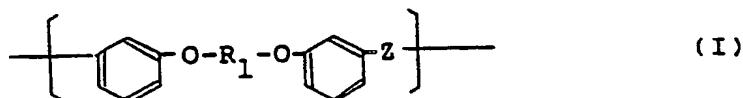
Table 1 (Cont'd)

	R e s i n   C o m p o s i t i o n (Parts by weight)			Softening point of uncured film [TMA method] (°C)	Tensile shear strength(kg/cm <sup>2</sup> )	
	Polymer (100 parts)		Bismaleimide compound (parts)		25 °C	240°C
	Diamine Compound (mole)	Tetracarboxylic dianhydride (mole)				
Ex. 14	2,2-Bis[4-(3-aminophenoxy)-phenyl]propane (0.1)	3,3',4,4'-Benzophenone-tetracarboxylic dianhydride (0.095)	4,4'-Bis(3-maleimido-phenoxy)biphenyl (50)	183	300	190
Ex. 15	Bis[4-(3-aminophenoxy)-phenyl]sulfide (0.1)	Pyromellitic dianhydride (0.092)	Bis[4-(3-maleimido-phenoxy)phenyl]sulfide (50)	181	290	205
Ex. 16	ditto (0.1)	3,3',4,4'-Benzophenone-tetracarboxylic dianhydride (0.09)	1,3-Bis(3-maleimido-phenoxy)benzene (50)	179	290	200
Ex. 17	1,3-Bis(3-aminophenoxy)-benzene (0.1)	ditto (0.098)	ditto (50)	167	295	190

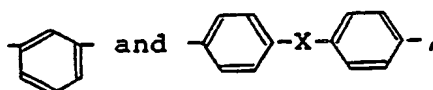
## Claims

1. A thermosetting resin composition comprising:

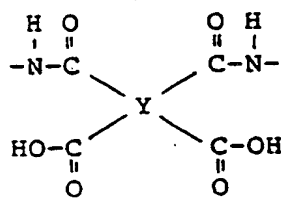
i) about 100 parts by weight of a polymer having recurring units represented by the formula (I):



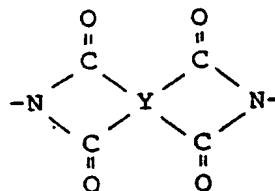
wherein  $\text{R}_1$  represents a divalent group selected from:



$\text{X}$  is selected from : a direct bond, divalent hydrocarbon groups containing from about 1 to about 10 carbon atoms, hexafluorinated isopropylidene groups, carbonyl groups, thio groups, sulfinyl groups, sulfonyl groups and oxo groups; and  $\text{Z}$  represents at least one compound selected from the group consisting of

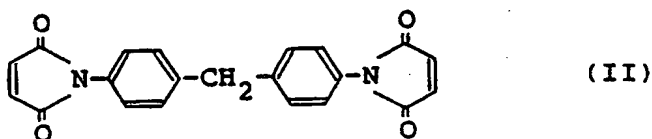


and

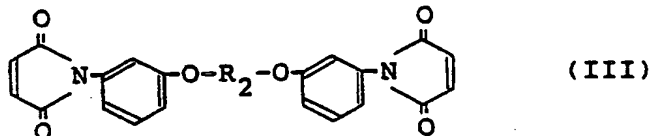


wherein  $\text{Y}$  represents a tetravalent group selected from : aliphatic groups having at least two carbon atoms, cycloaliphatic groups, monocyclic aromatic groups, fused polycyclic aromatic groups, and non-fused cyclic aromatic groups composed of aromatic groups bonded together directly or via a crosslink; and

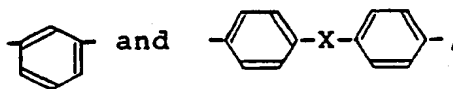
ii) from about 5 to about 100 parts by weight of a bismaleimide compound selected from: compounds of the formula (II):



and compounds of the formula (III):

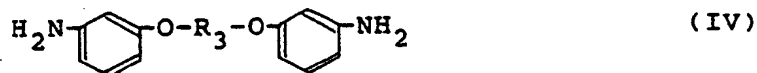


wherein  $\text{R}_2$  represents a divalent group selected from



5 X is selected from : a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, hexafluorinated isopropylidene groups, carbonyl groups, thio groups, sulfinyl groups, sulfonyl groups and oxo groups.

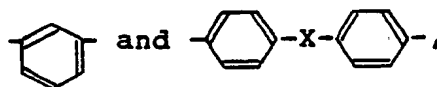
10 2. The thermosetting resin composition of claim 1, wherein said polymer is a polyamic acid prepared by reacting (a) a diamine compound of the formula (IV):



15

wherein R<sub>3</sub> represents a divalent group selected from

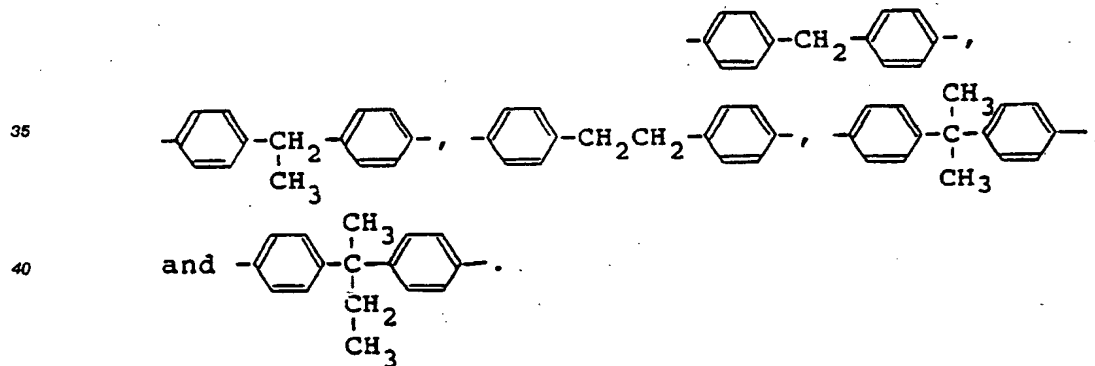
20



25 X is selected from : a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, hexafluorinated isopropylidene groups, carbonyl groups, thio groups, sulfinyl groups, sulfonyl groups and oxo groups, with (b) a compound selected from at least one tetracarboxylic dianhydride and a polyimide.

3. The resin composition of claim 2 wherein in said diamine compound of the formula (IV), R<sub>3</sub> is selected from:

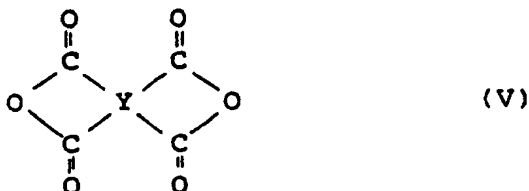
30



45

4. The resin composition of claim 2 or 3 wherein said tetracarboxylic dianhydride has the formula (V):

50

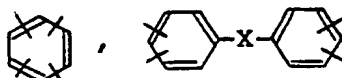


55

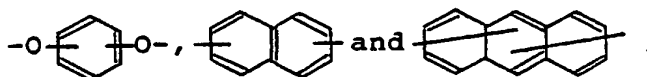
wherein Y is a tetravalent group selected from aliphatic groups having at least two carbon atoms, cycloaliphatic groups, monocyclic aromatic groups, fused polycyclic aromatic groups, and non-fused cyclic

aromatic groups.

5. The resin composition of claim 4 wherein Y is a tetravalent group selected from : aliphatic hydrocarbons having from 1 to 4 carbon atoms, cycloaliphatic hydrocarbons having from 4 to 8 carbon atoms,



10 wherein X is selected from the a direct bond, aliphatic hydrocarbons having from 1 to 4 carbon atoms, aliphatic hydrocarbons having from 1 to 4 carbon atoms substituted by from 1 to 6 fluorine atoms, -O-, -CO-, -S-, SO<sub>2</sub>-,



6. The resin composition of claim 2 wherein said diamine compound is selected from :

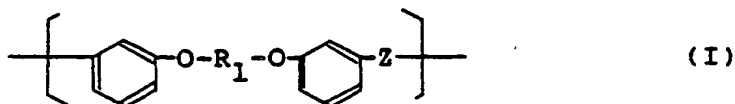
20 4,4'-bis(3-aminophenoxy)biphenyl, 2,2-bis[4-(3-aminophenoxy)phenyl]propane, bis[4-(3-aminophenoxy)phenyl] sulfite and 1,3-bis(3-aminophenoxy)benzene.

7. The resin composition of claim 2 wherein said tetracarboxylic dianhydride is selected from pyromellitic dianhydride and 3,3',4,4'-benzophenonetetracarboxylic dianhydride.

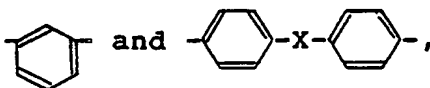
8. The resin composition of any preceding claim wherein said bismaleimide compound is selected from  
25 N,N'-4,4'-diphenylmethanebismaleimide, 4,4'-bis(3-maleimidophenoxy)biphenyl, 2,2-bis[4-(3-maleimidophenoxy)phenyl]propane, bis[4-(3-maleimidophenoxy)phenyl] sulfide and 1,3-bis(3-maleimidophenoxy)benzene.

9. A process for preparing a thermosetting resin composition comprising mixing

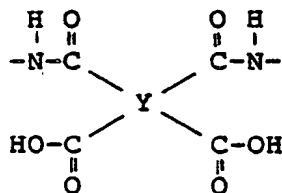
i) about 100 parts by weight of a polymer having recurring units represented by the formula (I):



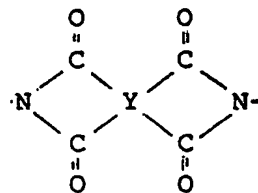
wherein R<sub>1</sub> represents a divalent group selected from



45 X is selected from: a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, hexafluorinated isopropylidene groups, carbonyl groups, thio groups, sulfinyl groups, sulfonyl groups and oxo groups, and Z represents at least one compound selected from :



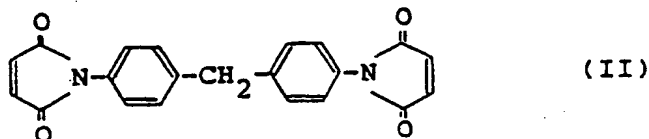
and



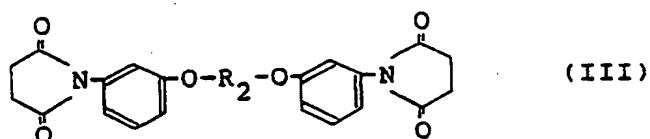
wherein Y represents a tetravalent group selected from aliphatic groups having at least two carbon atoms,

cycloaliphatic groups, monocyclic aromatic groups, fused polycyclic aromatic groups, and non-fused cyclic aromatic groups composed of aromatic groups bonded together directly or via a crosslink, and

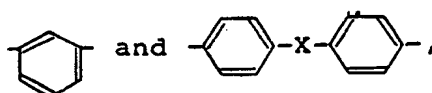
ii) from about 5 to about 100 parts by weight of bismaleimide compound selected from :  
compounds of the formula (II):



and compounds of the formula (III):



wherein R<sub>2</sub> represents a divalent group selected from



X is selected from: a direct bond, divalent hydrocarbon groups having from about 1 to about 10 carbon atoms, hexafluorinated isopropylidene groups, carbonyl groups, thio groups, sulfinyl groups, sulfonyl groups and oxo groups.

10. The process of claim 9 wherein said bismaleimide compound is dissolved in a polymer varnish prior to mixing with said polymer.

11. The process of claim 9 wherein said bismaleimide compound is dissolved in a polymer suspension prior to mixing with said polymer.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 89 30 4912

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X,P	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 275 (C-516)[3122], 29th July 1988; & JP-A-63 191 810 (SUMITOMO BAKELITE CO. LTD) 09-08-1988 * Abstract * ---	1,2,8,9	C 08 K 5/00 C 08 L 79/08 // (C 08 K 5/00 C 08 K 5:34 C 08 K 5:41 C 08 K 5:37 )
A	EP-A-0 107 897 (HITACHI CHEMICAL CO. LTD) * Claims * ---	1-7,10,11	
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 472 (C-551)[3319], 9th December 1988, page 75 C 516; & JP-A-63 54 435 (MITSUI TOATSU CHEM. INC.) 08-03-1988 * Abstract * -----	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 G C 08 K C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22-08-1989	Examiner GLANDDIER A.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	